S-Matrix Poles and the Second Virial Coefficient

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ABSTRACT

For cutoff potentials, a condition which is not a limitation for the calculation of physical systems, the S-matrix is meromorphic. We can express it in terms of its poles, and then calculate the quantum mechanical second virial coefficient of a neutral gas.

Here, we take another look at this approach, and discuss the feasibility, attraction and problems of the method. Among concerns are the rate of convergence of the 'pole' expansion and the physical significance of the 'higher' poles.

1 Introduction

This work has had a long gestation. Our earliest notes date from July 1976! At that time, two of us (M. Berrondo and S.Y. Larsen) obtained what we thought was an attractive formula for the q.m. second virial coefficient in terms of the location of its poles, as an alternative to its well known[1] and customary formulation in terms of phase shifts and bound state energies. Soon after doing this work, and obtaining some results, we were made aware that H. Nussenzveig had already published[2] an attractive article on the same subject and we stopped our efforts.

Recently, however, there has been interest in some other quarters[3], related to the pole expansion of the S-matrix, and we thought that useful details of such expansions might be properly be brought to light within the context of the statistical mechanics of the virial. Together with other colleagues, we look at the rate of convergence for phase shifts and for the virial. We look at asymptotic expansions for the poles. We try to see whether we can use tricks to either accelerate the convergence or sum background poles. We look at different model potentials. In the case of hard spheres, we obtain an expansion for the virial valid at low temperature.

2 The second virial in terms of the poles

For potentials decreasing faster than exponentials, like gaussian or cutoff potentials the Jost function is an entire function and, accordingly, the $\mathcal{S}$ matrix is meromorphic. We can express it as a exponential together with a product of poles :

$$\mathcal{S}_\ell(k) = e^{2i\delta_\ell} = (-)^\ell \; e^{-2ika} \; \prod_n \frac{k_{n,\ell}+k}{k_{n,\ell}-k} \;, \tag{1}$$

where a denotes the range of the potential and the $k_{n,\ell}$'s are the poles labelled in order of increasing modulus. It should be noted that this expression, apart from the factor $(-)^l$, which we will examine later, is equivalent to the one derived some years ago by Nussenzveig[4]

$$\mathcal{S}_\ell(k) = \; e^{-2ika} \; \prod_n \frac{k^*_{n,\ell}-k}{k_{n,\ell}-k} \;. \tag{2}$$

We recall that the original[5] quantum mechanical formulation of the Boltzmann part of second virial coefficient, in term of phase shifts and bound state energies, reads

$$(B_2)_{Boltz} = -2^{1/2}\lambda_T^3 \mathcal{N} \left[\sum_{B,\ell} (2\ell+1) e^{-2\beta k^2_{B,\ell}} + \frac{1}{\pi} \int_0^\infty dk \; e^{-2\beta k^2} \; \sum_\ell (2\ell+1) \frac{d}{dk} \delta_\ell(k) \right] \;, \tag{3}$$

where $\beta = 1/(\kappa T)$ in terms of the Boltzmann 's constant κ and the temperature T, λ_T denotes $h/\sqrt{2\pi m \kappa T}$ and $\mathcal{N}$ is the number of particles in the volume V. (Note that $2\beta = \lambda_T^2/(2\pi)$). The sum for the bound states runs over ℓ and the number of bound states for each ℓ.

In later calculations and formulations[6], a partial integration has often been performed to yield the virial in terms of the phase shifts, themselves, and the bound state energies. Also for convenience, we have divided the virial into two parts, a Boltzmann plus an exchange part. We focus on the Boltzmann part, but can at any moment obtain the exchange part by minor internal changes of sign and the inclusion of a perfect gas term.

Since the $\mathcal{S}$ matrix, here, has a compact expression in terms of its poles the previous equation also has such an expression. Indeed the derivative $d\delta_\ell/dk$ is nothing else than

$$\frac{d}{dk}\delta_\ell = -a + \frac{1}{2i}\sum_n \left[\frac{1}{k_{n,\ell}+k} + \frac{1}{k_{n,\ell}-k}\right] \ . \tag{4}$$

Introducing (4) in (3) we look at the contribution from the bracket

$$\sum_{B,\ell}(2\ell+1)e^{-2\beta k_{B,\ell}^2} + \frac{1}{\pi}\ \sum_l (2\ell+1)\left(-\frac{a}{2}\sqrt{\frac{\pi}{2\beta}} - \sum_n \frac{1}{i}\int_0^\infty dk\ e^{-2\beta k^2}\ \frac{k_{n,\ell}}{k^2-k_{n,\ell}^2}\right) \ . \tag{5}$$

The integral involving the pole expansion can be written in terms of the error function

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}}\int_0^z e^{-v^2}dv \ . \tag{6}$$

In Appendix A we show that

$$-\frac{k_{n,\ell}}{i}\int_0^\infty dk\ e^{-2\beta k^2}\ \frac{1}{k^2-k_{n,\ell}^2} = \frac{\pi}{2}e^{-2\beta k_{n,\ell}^2}\left(\mathrm{erf}(-ik_{n,\ell}\sqrt{2\beta}) \mp 1\right) \ , \tag{7}$$

with the sign - when the $\Im(k_{n,\ell})$ is positive and the sign + when the $\Im(k_{n,\ell})$ is negative. The bracket then reads

$$\sum_{B,\ell}(2\ell+1)e^{-2\beta k_{B,\ell}^2} + \ \sum_l (2\ell+1)\left(-\frac{a}{\sqrt{2}\sqrt{4\pi\beta}} + \frac{1}{2}\sum_n e^{-2\beta k_{n,\ell}^2}\left[\mathrm{erf}(-ik_{n,\ell}\sqrt{2\beta}) \mp 1\right]\right) \ . \tag{8}$$

We now put together the terms corresponding to bound states ($\sum_{B,\ell}$) and the terms corresponding to bound states, in the expression involving the poles ($\sum_{n,\ell}$). The poles involved in these terms are situated in the upper half plane $\Im(k) > 0$. According to our previous discussion, the exponential $\exp(-2\beta(k_{n,\ell})^2)$ is then weighted by the factor (-1/2). Combined with the exponential terms of the bound states, this yields the factor +1/2 as for the other poles. The bracket then reads

$$\sum_l (2\ell+1)\left(-\frac{a}{\sqrt{2}\sqrt{4\pi\beta}} \ + \frac{1}{2}\sum_n e^{-2\beta k_{n,\ell}^2}(\mathrm{erf}(-ik_{n,\ell}\sqrt{2\beta}) + 1)\right) \ . \tag{9}$$

Remembering, now, that $\mathrm{erf}(-z) = -\mathrm{erf}(z)$ and $1 - \mathrm{erf}(z) = \mathrm{erfc}(z)$, and using $2\beta = \lambda_T^2/(2\pi)$ we obtain our final expression (in terms of λ_T):

$$(B_2)_{Boltz} = -2^{1/2}\lambda_T^3\mathcal{N}\ \sum_l (2\ell+1)\left[-\frac{a}{\sqrt{2}\lambda_T} + \frac{1}{2}\sum_n \exp(-\frac{\lambda_T^2}{2\pi}k_{n,\ell}^2)\mathrm{erfc}(i\frac{\lambda_T}{\sqrt{2\pi}}k_{n,\ell})\ \right] \ . \tag{10}$$

3 The phase shifts in terms of poles

Clearly our procedure becomes more attractive if few poles are required to reproduce the second virial to good accuracy. In this section, we examine how the expansion, Eq.(4), reproduces the phase-shifts.

For a pure hard sphere potential, the answer is very pleasing: the number of poles for the $\ell^{\rm th}$partial wave equals ℓ.

For $\ell = 0$, the phase shift of a hard sphere of radius σ is just $-k\sigma$ and the poles do not contribute. For the higher ℓ's, we find that our formula for the S-matrix works perfectly, but that the factor $(-1)^\ell$ is not needed. We note that asymptotically the phases tend to $-k\sigma - \ell\pi/2$.

Unfortunately, for the more common cutoff potentials, the number of poles appearing in the expansion is infinite and, practically, to obtain the phase shift to, say 5 digits accuracy, the number of poles required is impressively large. We note, though, that except for poles found on the imaginary axis, they occur in pairs, in the third and fourth quadrant, and thus for these pairs, it is sufficient to determine the poles in the last quadrant. For a potential made up of a (repulsive) hard core plus an attached attractive square well, we find the results presented in table 1.

N	δ_0	$\mathcal{S}_0$
22	.067181	(.9909869, .1339585)
72	.073081	(.9893373, .1456426)
122	.074379	(.9889561, .1482090)
522	.076023	(.9884633, .1514605)
1022	.076312	(.9883756, .1520316)
2022	.076473	(.9883265, .1523510)
10022	.076620	(.9882818, .1526403)
50022	.076654	(.9882713, .1527083)
150022	.076661	(.9882693, .1527210)
Exact	.076664	(.9882682, .1527283)

Table 1. Poles for 1 antibound state + N pairs

This is for $\ell = 0$, $k\sigma = q = 0.1$, the de Boer parameter $\Lambda^* = (h^2/mV_0\sigma^2)^{1/2}$ equal to 10, the hard core radius σ and finally a, the outer limit of the attractive potential, equal to 2.85σ.

The expansion converges but so slowly that we are faced with the necessity of increasing the rate of convergence of the series. We note that at the origin ($k = 0$), the phase shift behaves like $k^{2\ell+1}$. Thus, for a given ℓ, derivatives up to 2ℓ are equal to zero. We obtain:

$$\begin{aligned} -a + \frac{1}{i}\sum_n \frac{1}{k_{n,\ell}} &= 0 \quad \text{for} \quad \ell \geq 1 \\ \sum_n \frac{1}{k_{n,\ell}^{2j+1}} &= 0 \quad 1 \leq j \leq \ell - 1 \text{ for } \quad \ell \geq 2\ . \end{aligned} \tag{11}$$

We can now try to accelerate the convergence of (4) by subtracting the terms above, multiplied by appropriate powers of k. We obtain, for $\ell \geq 1$,

$$\frac{d}{dk}\delta_\ell = \frac{1}{2i}\sum_n \left[\frac{1}{k_{n,\ell}+k} + \frac{1}{k_{n,\ell}-k} - \frac{2}{k_{n,\ell}}\sum_{j=0}^{\ell-1}\left(\frac{k}{k_{n,\ell}}\right)^{2j}\right] , \tag{12}$$

which can also be written as

$$\frac{d}{dk}\delta_\ell = \frac{1}{i}\sum_n \left(\frac{k}{k_{n,\ell}}\right)^{2\ell} \frac{k_{n,\ell}}{k_{n,\ell}^2 - k^2} . \tag{13}$$

We see that, for high orders, the terms behave as $1/(k_{n,\ell})^{2\ell+3}$.

Integrating the above equations with respect to k we find

$$\delta_\ell(k) = \delta_\ell(0) + \frac{1}{2i}\sum_n \left[\ln\left(\frac{k_{n,\ell}+k}{k_{n,\ell}-k}\right) - \sum_{j=0}^{\ell-1}\frac{2}{2j+1}\left(\frac{k}{k_{n,\ell}}\right)^{2j+1}\right] \qquad \ell \geq 1 . \tag{14}$$

For $\ell = 1, q = 0.1$ and 23 pairs of poles, we obtain $1.478248\ 10^{-3}$ compared to the exact result of $1.47826613\ 10^{-3}$ and, similarly, for $\ell = 2$, $4.04298921\ 10^{-6}$ instead of $4.042988889\ 10^{-6}$. The method, however, deteriorates as the energy increases.

To remedy the slow convergence for $\ell = 0$, we introduce the derivative of the phase shift (non zero) at $k = 0$, i.e.

$$\frac{d}{dk}\delta_0(k) = \frac{d}{dk}\delta_0(k)|_{k=0} + \frac{1}{2i}\sum_n \left[\frac{1}{k_{n,0}+k} + \frac{1}{k_{n,0}-k} - \frac{2}{k_{n,0}}\right]. \tag{15}$$

We then easily calculate the new term using trigonometric functions.

To prevent the deterioration as k increases, we limit the number of subtractions to 2. The results are then presented in table 2. Clearly, the number of poles required, ℓ being fixed, rises as the energy increases. On the other hand, at fixed energy, the number of poles needed is least when ℓ is largest.

$k\sigma$ ℓ	0	1	2	3	4	5	6
1	69	70	19	20	21	22	23
2	141	142	37	38	39	40	41
3	217	218	55	56	57	58	59
4	291	292	73	74	75	76	77
5	367	368	91	92	93	94	95
6	443	444	111	112	113	114	115
7	519	520	129	130	131	132	133
8	597	598	147	148	149	150	151
9	673	674	165	166	167	168	169
10	751	752	185	186	187	188	189

Table 2. Poles required for 5 digit accuracy

4 Asymptotic formulas

The simplest way to remedy a lack (or a limited number) of poles is to determine an asymptotic formula. Nussenzveig, in his book[4], derived such an asymptotic expression, which we extended to 'handle ' hard cores, but we need to increase its accuracy.

We begin by looking for an asymptotic formula for the s-wave, and then generalize to higher angular momenta. The zeros of the Jost function $F(k)$ are the poles of the S-matrix $F(-k)/F(k)$. They are given (see Appendix B) by solving the equation

$$\begin{aligned} e^{2ik(a-\sigma)} &= \frac{4k^2}{V(a)}\left[1+\frac{i}{2k}\left(2M-\frac{V'(a)}{V(a)}\right)\right. \\ &+ \left.\frac{1}{4k^2}\left(\frac{V''(a)}{V(a)}-\frac{V'(a)^2}{V(a)^2}-2V(a)+2M\frac{V'(a)}{V(a)}-2M^2\right)\right] , \end{aligned} \tag{16}$$

where M denotes $M=\int_\sigma^a V(r')\,dr'$ (for a potential finite at the origin put $\sigma=0$) and $V(a)$ is assumed different from zero.
We thus obtain some corrections to Nussenzveig's leading term, which were calculated from the equation:

$$e^{2ik(a-\sigma)} = \frac{4k^2}{V(a)} . \tag{17}$$

To get the correct value we first solve equation (16) by setting

$$k\ (a-\sigma) = n\pi - \epsilon\ \pi/2 - i\ \Delta\ , \tag{18}$$

where $\epsilon=0,1$ according to whether $V(a)$ is positive or negative, and, then iterating

$$e^{\ \Delta} = \frac{2(x_0-i\Delta)}{A}\ , \tag{19}$$

with $x_0=n\pi-\epsilon\ \pi/2$ and $A^2=|V(a)|(a-\sigma)^2$. The first correction is

$$\Delta_0 = \ln\frac{2x_0}{A}\ , \tag{20}$$

which corresponds to that of Nussenzveig. The third iteration, practically, provides us with the exact value so that

$$\Delta \simeq \Delta_2 = \ln\left[(2x_0-2i\ln((2x_0-2i\ln(2x_0/A))/A))\,/A\right]\ . \tag{21}$$

To get higher order corrections we have to include additional terms in (17), involving higher powers of $1/k$, and solve by iteration

$$e^{\ \Delta} = 2\ \frac{x_0-i\Delta}{A}\left[1+\frac{\alpha_1}{x_0-i\Delta}+\frac{\alpha_2}{(x_0-i\Delta)^2}+\cdots\cdots\right]\ , \tag{22}$$

with

$$\begin{aligned} \alpha_1 &= \frac{i(a-\sigma)}{4}\left(2M-\frac{V'(a)}{V(a)}\right) \\ \alpha_2 &= \frac{(a-\sigma)^2}{8}\left(\frac{V''(a)}{V(a)}-\frac{3}{4}\ \frac{V'(a)^2}{V(a)^2}-2V(a)+M\frac{V'(a)}{V(a)}-M^2\right) . \end{aligned} \tag{23}$$

To test the method for the potential that we used before (hard core + square well), we define $A = 2\pi(a-\sigma)/\Lambda^*$. An expansion in $1/k$ up to the 4^{th} order yields the results in table 3. We see that we are able to reproduce the exact results, for the higher poles, to 5 digits.

	n	$k_{n,0}$
appr.	20	(33.0670568,-2.5190331)
exact	20	(33.0670586,-2.5190330)
appr.	21	(34.7670884,-2.5459707)
exact	21	(34.7670900,-2.5459707)
appr.	22	(36.4669649,-2.5716312)
exact	22	(36.4669647,-2.5716312)
appr.	23	(38.1667055,-2.5961305)
exact	23	(38.1667061,-2.5961304)

Table 3. $\Lambda^* = 10, \;\; a/\sigma = 2.85$

For waves with higher values of ℓ, we show, in Appendix C, that we can generalize the approach of Appendix B, for example by setting the free Jost solution equal to

$$w_\ell(kr) = i^{\ell+1}\sqrt{\frac{\pi}{2}kr}\; H^{(1)}_{\ell+1/2}(kr) \; , \tag{24}$$

and proceeding in a manner similar to that used for $\ell = 0$.

In table 4, we examine the quality of our approximations for values of ℓ not equal to zero. Our results for $\ell = 1, 2$ are of comparable quality to those that we found for the $l = 0$. The key parameter is the ratio $\ell/k(a-\sigma)$. So long as it is small the asymptotic results will be good. We see that for large ℓ's, we have to proceed to a larger value of n, before the behaviour of the poles becomes asymptotic.

ℓ		$k_{23,\ell}$
1	appr.	(38.1758622,-2.5955925)
	exact	(38.1758614,-2.5955925)
2	appr.	(36.4956875,-2.5698867)
	exact	(36.4957008,-2.5698843)
3	appr.	(36.5243519,-2.56815261)
	exact	(36.5244255,-2.56813956)
4	appr.	(34.8672057,-2.53969925)
	exact	(34.8674660,-2.53965187)
5	appr.	(34.9169320,-2.5366040)
	exact	(34.9175873,-2.5365038)
6	appr.	(33.2864742,-2.5046694)
	exact	(33.2883530,-2.5045969)

Table 4. $\Lambda^* = 10, \;\; a/\sigma = 2.85$

When the potential has no hard core, we show, in Appendix C, that the asymptotic expression of the poles is obtained (in lowest order) from the solution of

$$e^{2ika} = (-)^{\ell} \frac{V(a)}{4k^2} \ . \tag{25}$$

We then recover the $(-)^{\ell}$ dependence, mentioned earlier by Nussenzveig[4]. This dependence disappears when the potential incorporates a hard core.

5 Virial

Noting, in the previous section, the necessity of accelerating the convergence of the pole expansion, we present here the formalism for doing this for the virial. Afterwards we will discuss the application to various potentials.

Given the slowness of the basic expansion in terms of poles, we modify the basic virial equations, proposing two different versions. In the first one we simply write

$$\left(\frac{d}{dk}\delta_\ell(k)\right)_{k=0} = -a + \frac{1}{i} \sum_n \frac{1}{k_{n,\ell}} \ , \tag{26}$$

and add and subtract this from the derivative expression. This yields:

$$\begin{aligned}(B_2)_{Boltz} &= -2^{1/2}\lambda_T^3 \mathcal{N} \left[\frac{1}{2^{1/2}\lambda_T} \left(\frac{d}{dk}\delta_0(k)\right)_{k=0}\right. \\ &+ \left.\frac{1}{2}\sum_{l,n}(2\ell+1)\left(\exp(-\frac{\lambda_T^2}{2\pi}k_{n,\ell}^2) \ \operatorname{erfc}(i\frac{\lambda_T}{\sqrt{2\pi}}k_{n,\ell}) + \frac{2^{1/2} i}{k_{n,\ell}\lambda_T}\right)\right] \ . \end{aligned} \tag{27}$$

We have used the fact that

$$\left(\frac{d}{dk}\delta_\ell(k)\right)_{k=0} = 0 \ \text{ for } \ \ell > 0 \ . \tag{28}$$

We can push this further, using Eq.(11) of our paper. We then find that

$$\begin{aligned}(B_2)_{Boltz} &= -2^{1/2}\lambda_T^3 \mathcal{N} \left[\frac{1}{2^{1/2}\lambda_T} \left(\frac{d}{dk}\delta_0(k)\right)_{k=0}\right. \\ &+ \frac{1}{2}\sum_{l,n}(2\ell+1)\exp(-\frac{\lambda_T^2}{2\pi}k_{n,\ell}^2) \ \operatorname{erfc}(i\frac{\lambda_T}{\sqrt{2\pi}}k_{n,\ell}) \\ &+ \left.\frac{i}{2^{1/2}\lambda_T}\left(\sum_{\ell,n}(2\ell+1)\frac{1}{k_{n,\ell}} + \sum_{\ell=2}^{\infty}(2\ell+1) \ \sum_n\sum_{j=1}^{\ell-1} \ (2j-1)!! \ (\frac{\pi}{\lambda_T^2})^j \ \frac{1}{k_{n,\ell}^{2j+1}}\right)\right] \ . \end{aligned} \tag{29}$$

Finally, what we calculate is this virial divided by that obtained classically for a pure hard core of radius σ, i.e.

$$(B_2^*)_{Boltz} = \frac{3}{2\pi\mathcal{N}\sigma^3} \ (B_2)_{Boltz} \ . \tag{30}$$

5.1 Hard spheres

We illustrate in table 5, how with a limited number of poles (about 20) we reproduce the 2^{nd} virial coefficient for hard spheres, over a range of relatively low temperatures, for which these formalisms are designed.

	$\lambda_T/\sigma = 1$		$\lambda_T/\sigma = 30$	
ℓ	BLK[6]	Poles	BLK[6]	Poles
0	.477464829276	.477464829276	.429718346348E+03	.429718346348E+03
1	.752348708365	.752348708365	.445367908873E+01	.445367908873E+01
2	.584467004923	.584467004923	.867588096488E-02	.867588096488E-02
3	.335935832978	.335935832978	.848769265246E-05	.848769265246E-05
4	.155466787903	.155466787903	.544399040752E-08	.544399040752E-08
5	.059852912973	.059852912973	.258124235604E-11	.258124235604E-11

Table 5. The hard sphere virial, from Eq.(29)

In Appendix D, we outline how we recover terms in a low temperature expansion (σ/λ_T small), a number of which are found in BLK.

5.2 Hard sphere + square well

For $\Lambda^* = 4$, the 2 particles have a bound state for $\ell = 0$ and one for $\ell = 1$. These bound states then dominate the very low temperature behaviour of these partial virials (i.e. for these angular momenta), and therefore for these virials. This is due to the large exponential terms that arise for large λ_T/σ. This already becomes evident for $\lambda_T/\sigma = 2$, and becomes more important for $\lambda_T/\sigma = 5, 10, 20, 30 \cdots$

Still, for $\lambda_T/\sigma = 2$, it is useful to see the virial calculated and displayed as function of the number of poles taken into account, for different values of ℓ. In table 6 we subtract the first derivative as in Eq. (27).

Here it is well to comment on our reference BLK. The authors BLK published results on hard spheres[6], many years ago, but not partial results for distinct values of ℓ, nor results for a hard sphere + a square well. Here, by BLK, we mean that one of the previous authors (SYL) is using some of the old programs and the old methods to obtain results which can be used to benchmark the use of the poles. These results, however, have not been obtained with the same need and desire for accuracy that the old work required. The programs have now been used with machines with smaller word lengths, the calculations done with larger meshes, etc. The values of the bound states have also been obtained from our work with the poles.

N ℓ	0	1	2	3
B+AB	-4.96245020	-13.49991189	9.568499294	
1	-5.38351004	-14.59384163	-13.71610648	7.071340875
2	-5.42559329	-14.70879231	-15.01832365	-8.916442069
5	-5.44089652	-14.75294247	-15.23836884	-10.22935288
10	-5.44304631	-14.75932474	-15.25610946	-10.27349937
20	-5.44347274	-14.76060000	-15.25890823	-10.27875744
50	-5.44355258	-14.76083933	-15.25936689	-10.27949972
100	-5.44355890	-14.76085827	-15.25940041	-10.27954958
200	-5.44355982	-14.76086106	-15.25940520	-10.27955649
300	-5.44355993	-14.76086137	-15.25940573	-10.27955725
400	-5.44355996	-14.76086145	-15.25940587	-10.27955744
BLK	-5.44355995	-14.7608616	-15.2594062	-10.2795575

Table 6. $\Lambda^* = 4$, $a/\sigma = 2.85$, $\lambda_T/\sigma = 2$.
The virial as a function of the number N of pairs, for different angular momenta. The contribution of bound (B) and antibound (AB) states is given separately at the beginning of the table.

Here it is well to comment on our reference BLK. The authors BLK published results on hard spheres[6], many years ago, but not partial results for distinct values of ℓ, nor results for a hard sphere + a square well. Here, by BLK, we mean that one of the previous authors (SYL) is using some of the old programs and the old methods to obtain results which can be used to benchmark the use of the poles. These results, however, have not been obtained with the same need and desire for accuracy that the old work required. The programs have now been used with machines with smaller word lengths, the calculations done with larger meshes, etc. The values of the bound states have also been obtained from our work with the poles.

This said, we present two tables, exclusively with poles, for $\Lambda^* = 10$ and $a/\sigma = 2.85$, for which there are no bound states. In table 7 we show, for $\ell = 0$, the convergence of the virial as a function of the number of pairs, for different values of λ_T/σ.

N λ_T/σ	1	2	5	10
AB	0.598187603	1.554449992	0.649915614	-20.719592323
1	0.503078797	1.357448734	0.454501918	-20.909727874
2	0.457717502	1.318856199	0.420668117	-20.942948517
5	0.434770286	1.301162611	0.404123797	-20.959343787
10	0.431866213	1.298475743	0.401489560	-20.961970746
20	0.431323513	1.297945047	0.400962083	-20.962497768
50	0.431225758	1.297847856	0.400865048	-20.962594781
100	0.431218271	1.297840377	0.400857571	-20.962602258
200	0.431217192	1.297839297	0.400856492	-20.962603337
300	0.431217071	1.297839177	0.400856371	-20.962603457
400	0.431217040	1.297839146	0.400856349	-20.962603488

Table 7. $\Lambda^* = 10$, $a/\sigma = 2.85$, $\ell = 0$

In the table 8, we sum over the angular momenta, up to $\ell = 7$, noting that the largest contribution for $\ell = 7$ is of the order of 10^{-7}, and show the convergence of the virial as a function of the number of pairs per ℓ, for different temperatures.

N λ_T/σ	1	2	5	10
AB	4.19599724	9.11116433	13.85909885	-5.12661171
1	10.80533807	15.47507182	8.97472495	-18.26521543
2	11.51743916	10.90069896	-0.65662473	-28.69768995
5	2.21953160	0.10665942	-10.39425326	-38.23655996
10	1.33830379	-0.58575152	-11.05109579	-38.88877474
20	1.25987331	-0.66118370	-11.12575192	-38.96332180
50	1.25055050	-0.67043615	-11.13498509	-38.97255257
100	1.24998520	-0.67100089	-11.13554949	-38.97311816
200	1.24991013	-0.67107586	-11.13562419	-38.97319073
300	1.24990207	-0.67108401	-11.13563272	-38.97319829
400	1.24990001	-0.67108599	-11.13563474	-38.97320208

Table 8. The complete Boltzmann virial

5.3 Further comments on the poles

As we saw, if the discontinuity in the potential at the cut-off a is not zero, and also not infinite, then our asymptotic expansions, for the location of the poles which appear in the expression of the S-matrix, show that the number of these poles is infinite.

Alternatively, we can use an elegant argument, of Newton[7] and Nussenzveig[4], which argues that the function $G(k) = F(k)F(-k)$, involving the Jost function $F(k)$, is an entire function of the variable k^2, of order $1/2$, and therefore has an infinite number of zeroes, which then again leads to the conclusion that the S-matrix has an infinite number of poles. The basic element in both approaches is an analysis of the behaviour of the function $G(k)$ for large values of $|k|$.

As we can see directly, from our asymptotic expressions, the zeroes of $F(k)$, for these large values of $|k|$, depend on the value of the potential at a, rather than on the values for r from 0 to a. Thus, as already noted by Nussenzveig, the resulting poles do not have much physical significance. He shows that a Yukawa-type potential yields a branch cut, which if the potential is cut off, is replaced by an infinite set of poles.

One further point. We can readily understand that some of the poles represent bound states and resonances. In general, it is subtle to understand the physical significance of the poles. Nussenzveig dedicates a chapter in his book (Causality and Dispersion Relations) to this purpose. We commend it to our readers.

6 Conclusion

We think that the development of a formalism for the second virial coefficient, in terms of the poles of the S-matrix, is an attractive one. It is a formalism equally as powerful as the more conventional one, based on phase shifts and bound states, but, for example, treats the phase shifts and bound state contributions in a unified way.

For hard spheres, the number of poles for each ℓ is finite and we see that, with a handful of these poles, we can reproduce results obtained by previous methods.

For other more realistic potentials, and our hard sphere + square well, the number of poles is infinite and the phase shifts and the virial converge slowly in terms of the poles. We have, however, been able to devise tricks to accelerate this convergence. We have also perfected and extended the use of asymptotic expressions for the location of the poles. The result is that we can still obtain (and have obtained) results with a modest (non forbidding) number of poles.

These days, with the abundance of numerical power available, and the new methods that have been developed to locate poles[3] for realistic potentials, we are freer to choose the methods that we might use for virial calculations.

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Appendix A

The integrals in (5) are of the type

$$\int_0^\infty dk\ e^{-2\beta k^2}\ \frac{k_n}{k^2 - k_n}\ , \tag{A1}$$

where we drop, for convenience, the subscript ℓ in the expression of the $k_{n,\ell}$'s.

Now,let

$$I(\lambda) = e^{-\lambda k_n^2}\ \int_0^\infty dk\ e^{-\lambda k^2}\ \frac{1}{k^2 - k_n^2}\ . \tag{A2}$$

The function $I(\lambda)$ satisfies

$$\frac{d}{d\lambda} I(\lambda) = -e^{\lambda k_n^2} \frac{\sqrt{\pi}}{2\sqrt{\lambda}}\ . \tag{A3}$$

We have therefore

$$I(\lambda) = I(0) - \frac{\sqrt{\pi}}{2} \int_0^\lambda\ d\lambda' e^{\lambda' k_n^2} \frac{1}{\sqrt{\lambda'}}\ . \tag{A4}$$

Introducing

$$\mathrm{erf}(z) = \frac{2}{\sqrt{\pi}} \int_0^z e^{-v^2} dv\ , \tag{A5}$$

we have

$$I(\lambda) = \int_0^\infty dk \frac{1}{k^2 - k_n^2} - \frac{\pi}{2k_n} \mathrm{erf}(-i\sqrt{2\beta k_n})\ . \tag{A6}$$

By using the residues, note that

$$\begin{aligned} \int_0^\infty dk \frac{1}{k^2 - k_n^2} \quad &= \quad +\frac{\pi i}{2k_n}\ \Im(k_n) > 0 \\ & \qquad -\frac{\pi i}{2k_n}\ \Im(k_n) < 0\ , \end{aligned}$$

and thus

$$-\frac{k_{n,\ell}}{i} \int_0^\infty dk\ e^{-2\beta k^2}\ \frac{k_{n,\ell}}{k^2 - k_{n,\ell}^2} = \frac{\pi}{2} e^{-2\beta k_{n,\ell}^2} \Big(\mathrm{erf}(-ik_{n,\ell}\sqrt{2\beta}) \mp 1 \Big)\ , \tag{A7}$$

with the sign - when $\Im(k_{n,\ell})$ is positive and the sign + when $\Im(k_{n,\ell})$ is negative.

Appendix B

Here, we derive an asymptotic expression for the location of the poles of the $\mathcal{S}$ matrix,or, equivalently of the zeros of the Jost function (the zeros of the Jost function $F(k)$ are the poles of the S-matrix $F(-k)/F(k)$). We solve a Volterra equation, which generates the Jost solution $f_\ell(k,r)$ and, then, the Jost function. The latter $F_\ell(k) = f_\ell(k,\sigma)$ for a potential which includes a hard core and $F_\ell(k) = \lim_{r\to 0}(-kr)^\ell f_\ell(k,r)/(2\ell-1)!!$ otherwise. We recall that $f_\ell(k,r)$ is defined by the Cauchy condition:

$$\lim_{r\to\infty} f_\ell(k,r)\ \exp(-ikr) = i^\ell\ .$$

This gives us a Jost function which is analytic in the upper half plane $\Im(k) > 0$.

For $\ell = 0$, let be $g(k,r) = f_0(k,r)\ \exp(-ikr)$. The function g satisfies

$$g(k,r) = 1 - \frac{i}{2k}\int_r^\infty \left(e^{2ik(r'-r)} - 1\right)\ V(r')\ g(k,r')\ dr'\ . \qquad (B1)$$

As usual[7], writing $g(k,r)$ as a series $g(k,r) = \sum g_n(k,r)$, we note that it is absolutely and uniformly convergent when the potential V satisfies $\int_0^\infty r\ V(r)\ dr < \infty$. We construct the g_n by the recursive procedure

$$\begin{aligned} g_0(k,r) &= 1 \\ g_n(k,r) &= -\frac{i}{2k}\int_r^\infty \left(e^{2ik(r'-r)} - 1\right)\ V(r')\ g_{n-1}(k,r')\ dr'\ n \geq 1\ . \end{aligned}$$

We then obtain for a finite range potential, infinitely differentiable at the left of its cutoff denoted a, the terms

$$\begin{aligned} g_1(k,r) &= \frac{i}{2k}\int_r^a V(r')\ dr' \\ &\quad -\frac{1}{4k^2}e^{2ik(a-r)}\left(V(a) - \frac{V'(a)}{2ik} + \frac{V''(a)}{(2ik)^2} + \cdots\right) \\ &\quad +\frac{1}{4k^2}\left(V(r) - \frac{V'(r)}{2ik} + \frac{V''(r)}{(2ik)^2} + \ \cdots\right)\ , \end{aligned}$$

and

$$\begin{aligned} g_2(k,r) &= -\frac{1}{8k^2}\left(\int_r^a V(r')\ dr'\right)^2 \\ &\quad -\frac{1}{8k^4}e^{2ik(a-r)}\left(V(a)^2 - 3\frac{V'(a)\ V(a)}{(2ik)} + \cdots\right) \\ &\quad -\frac{1}{8ik^3}\left(V(r)\ \int_r^a V(r')\ dr' + \frac{2\ V^2(r) - V'(r)\ \int_r^a V(r')dr'}{2ik} + \cdots\cdots\cdots\right) \\ &\quad -\frac{1}{16k^4}e^{2ik(a-r)}\left(V(a) - \frac{V'(a)}{2ik} + \cdots\right)\left(V(r) + \frac{V'(r)}{2ik} + \cdots\right) \\ &\quad +\frac{i}{8k^3}e^{2ik(a-r)}\left(V(a) - \frac{V'(a)}{2ik} + \cdots\right)\int_r^a V(r')\ dr' \end{aligned}$$

$$+\frac{i}{8k^3}\int_r^a V(r')\left(V(r')-\frac{V'(r')}{2ik}+\cdots\right)dr'$$
$$+\frac{1}{16k^4}\left(V(a)-\frac{V'(a)}{2ik}+\frac{V''(a)}{(2ik)^2}\cdots\right)\left(V(a)+\frac{V'(a)}{2ik}+\frac{V''(a)}{(2ik)^2}\cdots\right) ,$$

etc.. and

$$g_3(k,r)=\frac{1}{32k^4}\, e^{2ik(a-r)}\left[\, V(a)\, \left(\int_r^a V(r')\, dr'\right)^2 + O(k^{-1})\right] + O(k^{-3}) \; .$$

To obtain the g_n's, we have used partial integration on the factor containing the exponential and differentiated the term containing the potential.

If one approximates the function $g(k,r)$ by the sum $s(k,r)=g_0+g_1+g_2+g_3$, the Jost function is approximated by $s(k,0)$, for a potential which is finite at the origin, and by $s(k,\sigma)\exp(ik\sigma)$ for a potential which includes a hard core component. We obtain, setting $M=\int_\sigma^a V(r')dr'$,

$$\begin{aligned} e^{2ik(a-\sigma)} &= \frac{4k^2}{V(a)}\left[1+\frac{i}{2k}\left(2M-\frac{V'(a)}{V(a)}\right)\right. \\ &+ \left.\frac{1}{4k^2}\left(\frac{V''(a)}{V(a)}-\frac{V'(a)^2}{V(a)^2}-2V(a)+2M\frac{V'(a)}{V(a)}-2M^2\right)\right] , \end{aligned}$$

as the condition which will yield the poles of the $\mathcal{S}$ matrix, provided that $V(a)\neq 0$.

Appendix C

For higher waves we have to deal with the following free Jost solution

$$w_\ell(kr) = i(-)^\ell \sqrt{\frac{\pi}{2} kr}\ H^{(1)}_{\ell+1/2}(kr)\ , \qquad (C1)$$

where $H^{(1)}_\nu$ is the Hankel function of the first kind of order ν. We have

$$\lim_{r\to 0} (kr)^\ell\ w_\ell(kr) = (-)^\ell\ (2\ell - 1)!!\ ,$$

and

$$\lim_{r\to\infty} \exp(-ikr)\ w_\ell(kr) = i^\ell\ .$$

The w_ℓ's are simply given by [8]

$$w_\ell(kr) = i^\ell e^{ikr} P_\ell(kr)\ , \qquad (C2)$$

where the P_ℓ's denote the polynomial part of the Hankel, i.e.

$$P_\ell(kr) = \sum_{m=0}^{\ell} \frac{(l+m)!}{(l-m)!m!} \left(\frac{i}{2kr}\right)^m\ . \qquad (C3)$$

We proceed in a manner similar to that used for $\ell = 0$. We introduce

$$g_\ell(k,r) = f_\ell(k,r)/w_\ell(kr)\ , \qquad (C4)$$

where $f_\ell(k,r)$ is the Jost solution having the appropriate behaviour for r tending to infinity

$$\lim_{r\to\infty} i^\ell \exp(-ikr)\ f_\ell(k,r) = 1\ .$$

Note that the w_ℓ's never vanish for k real. The function g_ℓ then satisfies

$$\begin{aligned} g_\ell(k,r) &= 1 - \frac{i}{2k} \int_r^\infty (e^{2ik(r'-r)} P_\ell(kr')^2 \frac{P_\ell(-kr)}{P_\ell(kr)} \\ &- P_\ell(kr')\ P_\ell(-kr'))V(r') g_\ell(k,r')\ dr'\ . \end{aligned}$$

We apply the previous procedure (see Appendix B) which consists in using partial integration for the factor containing the exponential and differentiating the term containing the potential $V(r')$ multiplied by $P_\ell^2(kr')$.

When the potential includes an hard core component the factors $(kr')^{-m}$ $m > 0$, occurring in the polynomial P_ℓ, are bounded by $(k\sigma)^{-m}$ and therefore goes to zero when $|k|$ tends to infinity.

We then obtain a formula similar to (15) but where successive derivatives of P_ℓ appear. This implies additional ℓ-dependent terms in the expansion in powers of $1/k$.

For example, for the potential used before (hard core plus square well) we found,

$$
\begin{aligned}
e^{2ik(a-\sigma)} &= -\frac{4k^2(a-\sigma)^2}{A^2}\left[1+\frac{i}{k(a-\sigma)}\left(\frac{x}{b(b+1)}-A^2\right)\right. \\
&+ \frac{1}{2k^2(a-\sigma)^2}\left(-A^4+2A^2\frac{x}{b(b+1)}+A^2-x\frac{2b^2+x}{b^2\,(b+1)^2}\right) \\
&+ \frac{i}{6k^3(a-\sigma)^3}\left(-\frac{3}{2}A^4+A^6-3A^4\frac{x}{b(b+1)}+3x\frac{A^2}{b^2(b+1)^2}(2b^2+x)\right. \\
&+ \left.\left.\frac{x}{2b^3(1+b)^3}\left(-6(1+b)^3+18b^3+x(1+3b-9b^2)-2x^2\right)\right)\right] ,
\end{aligned}
$$

where $A = 2\pi(a-\sigma)/\Lambda^*$; $x = \ell(\ell+1)$ and $b = \sigma/(a-\sigma)$.

When the potential has no hard core, the factors $1/(kr)^m$ $m > 0$ occurring in the P_ℓ's are no longer bounded and we have to reason differently.

In fact, when r tend to zero the term

$$
\frac{P_\ell(-kr)}{P_\ell(kr)} ,
$$

tends to $(-)^\ell$ and, in so far as the leading term of g_ℓ is concerned, we are left with

$$
\begin{aligned}
g_\ell(k,r) &= 1-\frac{i}{2k}\int_r^\infty ((-)^\ell e^{2ik(r'-r)}P_\ell(kr')^2\frac{1+ikr+\ldots}{1-ikr+\ldots} \\
&- P_\ell(kr')\;P_\ell(-kr'))V(r')\;dr' .
\end{aligned}
$$

When $|k|$ is large, only the behaviour of the potential at its cutoff a dominates

$$
g_\ell(k,r) = 1-(-)^\ell\frac{V(a)}{4k^2}e^{2ika} , \tag{C5}
$$

and the leading asymptotic expression is given by solving

$$
e^{2ika} = (-)^\ell\frac{V(a)}{4k^2} . \tag{C6}
$$

We then recover the alternating sign, which depends on whether ℓ is even or odd, mentioned earlier by Nussenzveig[4]. This dependence disappears when the potential incorporates a hard core.

Appendix D

We examine the low temperature expansion of the virial for a pure hard core. We start from the equation (10), which for the hard sphere reads:

$$(B_2)_{Boltz} = -2^{1/2}\lambda_T^3\mathcal{N}\ \sum_\ell (2\ell+1)\left[-\frac{\sigma}{\sqrt{2}\lambda_T}+\frac{1}{2}\sum_n \exp(-\frac{\lambda_T^2}{2\pi}k_{n,\ell}^2)\mathrm{erfc}(i\frac{\lambda_T}{\sqrt{2\pi}}k_{n,\ell})\right]\ . \quad (D1)$$

The equation (D1) involves the function $\exp(-z^2)\ \mathrm{erfc}(iz)$, where $z=\lambda_T\ k_{n,\ell}/\sqrt{2\pi}$. This latter has the asymptotic expression for λ_T/σ (or equivalently z) large

$$\exp(-z^2)\ \mathrm{erfc}(iz) = -\frac{i}{\sqrt{\pi}\ z}\left[1+\sum_{j=1}^{\infty}\frac{(2j-1)!!}{(2z^2)^j}\right]\ . \quad (D2)$$

Incorporating (D2), written for $z=\lambda_T\ k_{n,\ell}/\sqrt{2\pi}$, into (D1) we have:

$$\begin{aligned}(B_2)_{Boltz} &= -2^{1/2}\lambda_T^3\mathcal{N}\ \left[-\frac{\sigma}{\sqrt{2}\lambda_T}+\sum_{\ell\neq 0}(2\ell+1)\left(-\frac{\sigma}{\sqrt{2}\lambda_T}\right.\right.\\ &- \left.\left.\frac{i}{\sqrt{2}\lambda_T}\ \sum_{n=1}^{\ell}\left[\frac{1}{k_{n,\ell}}+\sum_{j=1}^{\infty}\frac{(2j-1)!!}{k_{n,\ell}^{2j+1}}\ \frac{\pi^j}{\lambda_T^{2j}}\right]\right)\right]\ .\end{aligned}$$

In the previous equation use is made of the property for hard spheres the $\mathcal{S}$ matrix has no poles for $\ell=0$ and exactly ℓ poles for $\ell\neq 0$.

The expression for the virial, divided by its classical limit, as in (30) reads:

$$\begin{aligned}(B_2^*)_{Boltz} &= \frac{3}{2\pi}\left(\frac{\lambda_T}{\sigma}\right)^2\left[1+\sum_{\ell\neq 0}(2\ell+1)\left(1+\sum_{n=1}^{\ell}\frac{i}{(k_{n,\ell}\ \sigma)}\right.\right.\\ &+ \left.\left.\sum_{j=1}^{\infty}(2j-1)!!\ (-)^j\ \pi^j\left(\frac{\sigma}{\lambda_T}\right)^{2j}\ \sum_{n=1}^{\ell}\left(\frac{i}{(k_{n,\ell}\ \sigma)}\right)^{2j+1}\right)\right]\ .\end{aligned}$$

The calculation of the virial requires the knowledge of the sums

$$S_{j,\ell} = \sum_{n=1}^{\ell}\left(\frac{i}{(k_{n,\ell}\ \sigma)}\right)^{2j+1} \qquad j\leq 1\ . \quad (D3)$$

The poles $k_{n,\ell}$ of the $\mathcal{S}$ matrix are the zeros of the polynomial part of the Hankel function (Eq.(C3) for $r=\sigma$). Introducing $x_{n,\ell}=i/(k_{n,\ell}\ \sigma)$, these latter are roots of the polynomial

$$P(x) = \sum_{m=0}^{\ell} a_{m,\ell}\ x^m\ , \quad (D4)$$

with

$$a_{m,\ell} = \frac{(l+m)!}{2^m\ (l-m)!m!}\ . \quad (D5)$$

The sums $S_{j,\ell}$, Eq.(D3), are given by

$$S_{j,\ell} = \sum_{n=1}^{\ell} x_{n,\ell}^{2j+1} \qquad j \leq 1 \ , \tag{D6}$$

in terms of the roots of the polynomial Eqs. (D4,D5).

They obey the recursion formula

$$S_{1,\ell} = -\frac{a_{\ell-1,\ell}}{a_{\ell,\ell}}$$

$$S_{j,\ell} = -\sum_{m=1}^{j-1} \frac{a_{\ell-m,\ell}}{a_{\ell,\ell}} \ S_{m,\ell} - j \ \frac{a_{\ell-j,\ell}}{a_{\ell,\ell}} \qquad j \geq 2 \ . \tag{D7}$$

From (D5) and (D7) we find, after calculation,

ℓ	$S_{1,\ell}$	$S_{3,\ell}$	$S_{5,\ell}$	$S_{7,\ell}$	$S_{9,\ell}$	$S_{11,\ell}$
1	-1	-1	-1	-1	-1	-1
2	-1	0	1/9	1/27	0	$-1/243$
3	-1	0	0	$-1/225$	$-1/1125$	$-1/16875$
4	-1	0	0	0	1/11025	1/77175
5	-1	0	0	0	0	$-1/893025$

The sums $S_{2j+1,\ell}, j \neq 0$ are zero for $\ell \geq j+1$.

Rewriting $(B_2^*)_{Boltz}$ in terms of the $S_{j,\ell}$'s

$$(B_2^*)_{Boltz} = \frac{3}{2\pi} \ \frac{\lambda_T^2}{\sigma^2} \left[1 + \sum_{j=1}^{\infty} (2j-1)!! \ (-)^j \ \pi^j \left(\frac{\sigma}{\lambda_T}\right)^{2j} \ \sum_{\ell \neq 0} (2\ell+1) \ S_{2j+1,\ell} \right] \ , \tag{D8}$$

and, taking into account the results depicted in the table, we have

$$\begin{aligned} (B_2^*)_{Boltz} \ &= \ \frac{3}{2\pi} \ \frac{\lambda_T^2}{\sigma^2} \left[1 + 3\pi \left(\frac{\sigma}{\lambda_T}\right)^2 - \frac{22}{3} \ \pi^2 \ \left(\frac{\sigma}{\lambda_T}\right)^4 + \frac{1921}{45} \pi^3 \left(\frac{\sigma}{\lambda_T}\right)^6 - \frac{165673}{525} \pi^4 \left(\frac{\sigma}{\lambda_T}\right)^8 \right. \\ &+ \ \left. \frac{472102277}{165375} \ \pi^5 \left(\frac{\sigma}{\lambda_T}\right)^{10} + \dots \right] \ . \end{aligned}$$

We thus recover the first terms extracted by BLK.

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